544, 252

PATENT COOPERATION TREATY

REC'D 04 OCT 2005
WIPO PCT

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P60184PCT	FOR FURTHER ACTION See Form PCT/IPEA/416	
International application No. PCT/EP2004/002208	International filing date *(day/month/year)* 04.03.2004	Priority date *(day/month/year)* 10.03.2003
International Patent Classification (IPC) or national classification and IPC C25D7/12, C25D5/18, H05K3/24		
Applicant ATOTECH DEUTSCHLAND GMBH et al		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 8 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 2 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☒	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
20.09.2004	29.09.2005
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Zech, N Telephone No. +31 70 340-2915

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/002208

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages	
1-30	as originally filed
Claims, Numbers	
2-11	as originally filed
12-17	received on 26.10.2004 with letter of 20.10.2004
1	received on 09.08.2005 with letter of 05.08.2005
Drawings, Sheets	
1/7-7/7	as originally filed

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/002208

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-17
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-17
Industrial applicability (IA)	Yes:	Claims	1-17
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

D1: US 2003/010642 A1 (TAYLOR E JENNINGS ET AL) 16 January 2003 (2003-01-16)
D4: EP-A-1 069 212 (APPLIED MATERIALS INC) 17 January 2001 (2001-01-17)
D5: US-A-6 132 584 (HUBEL EGON) 17 October 2000 (2000-10-17)
D6: EP-A-0 568 728 (ATOTECH DEUTSCHLAND GMBH) 10 November 1993 (1993-11-10)
D8: GB 2 101 159 A (NAPCO INC) 12 January 1983 (1983-12-01)
D9: US 6 238 529 B1 (JENS GEISSLER ET AL) 29 May 2001 (2001-05-29)

2 Novelty

The present application does meet the criteria of Article 33(1) PCT, because the subject-matter of claim 1 is new in the sense of Article 33(2) PCT.

2.1 The document D8 seeks to improve the filling of high-aspect ratio structures for high current density plating methods (D8, page 3, lines 14-19; page 4, line 130 - page 5, line 4). For this purpose in document D8 is disclosed a method for the electroplating of high-aspect ratio structures which comprises a velocity component normal to the surface of the workpiece of about 10 m/sec (D8, figure 6; page 4, lines 113-129).

Since the method is expressed as a "high current density plating method" without any mentioning of pulse reverse current the present subject matter of claim 1 is new.

2.2 Document D1 (paragraphs 32, 40-45, 78, 101, 102; figure 2) discloses a method for electroplating high-aspect ratio through holes with a pulse reverse current flow having

e.g. a frequency of 5 Hertz in each cycle.

The subject-matter of claim 1 differs from this known high-aspect structure plating method in that during plating the workpiece is brought into contact with an electrolyte with a velocity component normal to the surface of at least 1 m/sec.

2.3 Document D4 (paragraphs 8, 11, 13, 28-30, 41) discloses a method for electroplating high-aspect ratio blind holes with a pulse reverse current flow where the duration of the forward cycle is 4 to 16 seconds and the duration of the reverse cycle is 0.3 seconds; thus the frequency of the whole cycle with forward and reverse pulse is less than 6 Hertz and the ratio of forward to reverse cycle duration is in-between 13 and 53. Usually the electrolyte flow impinges perpendicularly on the substrate plating surface during operation of the cell.

The subject-matter of claim 1 differs from this known high-aspect structure plating method in that during plating the workpiece is brought into contact with an electrolyte with a velocity component normal to the surface of at least 1 m/sec (while in document D4 no indication is given of how strong the velocity is).

2.4 The document D5 shows a method for electroplating printed circuit boards wherein the workpiece is brought into contact with an electrolyte with a velocity component normal to the surface of while simultaneously applying a pulse reverse current flow (D5, column 2, lines 18-52; column 4, lines 33-50; figure 1).

The subject-matter of claim 1 differs from this known high-aspect structure plating method in that the frequency is between 10 and 10'000 Hertz and the value of the normal component of the velocity is not expressed.

2.5 The document D6 shows a method for electroplating within high-aspect ratio structures wherein the workpiece is brought into contact with an electrolyte with a velocity component normal to the surface of over 5 m/sec while simultaneously applying a pulse reverse current flow (D6, claims 1-4 and 8; figures 1-4).

The subject-matter of claim 1 differs from this known high-aspect plating method in that

the frequency is considerably higher than 6 Hertz (according to claims 1-3 and page 10, line 8 of D1, where a preferred maximal cycle duration is about 3000 µsec (50 µsec + 30*50 µsec, which corresponds to a preferred minimal frequency of 645 Hertz when plating a hole with an aspect ratio of 1).

3 Inventive step and clarity

3.1 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claim 1 does not involve an inventive step in the sense of Article 33(3) PCT. Furthermore, the application does not meet the requirements of Article 6 PCT, because said claim is not clear.

The document D8 seeks to improve the filling of high-aspect ratio structures for high current density plating methods (D8, page 3, lines 14-19; page 4, line 130 - page 5, line 4). For this purpose in document D8 is disclosed a method for the electroplating of high-aspect ratio structures which comprises a velocity component normal to the surface of the workpiece of about 10 m/sec (D8, figure 6; page 4, lines 113-129). The present application is not inventive over said method for the following reasons:

In the present independent claim 1 a plating method using pulse conditions with an open range is disclosed. Said open range is such that in its extreme extrapolation (frequency much smaller than 6 Hertz and ratio of duration of forward current to reverse current much higher than 5) a (near-)direct current application is included. Thus, the claimed subject matter appears not inventive - at least not for the entire claimed range - because direct current methods are known, see D8, and would be recognised by a person skilled in the art to have the same effect as a "near"-direct current method i.e. a method according to present claim 1 where the frequency is much smaller than 6 Hertz, i.e. ≈ 0, and the ratio of duration of forward current to reverse current much higher than 5, i.e. $\approx \infty$, thus about DC. Thus, the results of such "near"-direct current conditions would be expected to be similar to the one shown in the comparable example for DC conditions in Table 2 of present description.

3.2 From this (item 3.1) follows that an essential feature is missing that limits the open range as set out in present claim 1. The following feature could probably serve to define the invention in a more clear way:

(1) ratio of the duration of forward current pulses to the duration of the reverse current pulses of one cycle is set in the range from 5 to 75 according to present claim 2.

Since independent claim 1 does not contain this feature it does not meet the requirement following from Article 6 PCT taken in combination with Rule 6.3(b) PCT that any independent claim must contain all the technical features essential to the definition of the invention.

3.1 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claim 1 or claim 1 in combination with claim 2 does not involve an inventive step in the sense of Article 33(3) PCT. Furthermore, the application does not meet the requirements of Article 6 PCT, because said claim is not clear.

Document D4 (paragraphs 8, 11, 13, 28-30, 41) discloses a method for electroplating high-aspect ratio blind holes with a pulse reverse current whereby the filled structures are void-free respectively seam-free (this is clearly shown in D4, paragraphs 10-13, 18, 26, 35, 41). The applied pulse reverse current flow comprises a duration of the forward cycle of 4 to 16 seconds and a duration of the reverse cycle of 0.3 seconds; thus the frequency of the whole cycle with forward and reverse pulse is less than 6 Hertz and the ratio of forward to reverse cycle duration is in-between 13 and 53. The electrolyte flow impinges perpendicularly on the substrate plating surface during operation of the cell. In document D4, col. 2, lines 43-45 an electrolyte flow is mentioned which may impinge perpendicularly on the substrate surface during the operation without further specifying the velocity.

Thus, the subject-matter of the combination of claim 1 and 2 differs from this known high-aspect structure plating method in that during plating the workpiece is brought into contact with an electrolyte with a velocity of at least 1 m/sec.

The problem to be solved by the present invention may therefore be regarded as

achieving a sufficient metal plating thickness in the holes with high-aspect ratio and at the same time a metal deposit as even and efficient as possible (according page 3, paragraph 2 and 3 of present application).

Since it is known from other prior art documents, such as D9 (col. 1, lines 6-11; col. 3, lines 16-29; col. 4, lines 7-13; col. 7, lines 38-40; col. 8, lines 53-67; figures), that the throwing power and plating uniformity can be improved by applying an electrolyte flow normal to the substrate surface, it is obvious that such a measure would most probably lead at the same time to a void-free fill of the high-aspect ratio structures while the throwing power and uniformity of plating thickness is improved too. It thus would be obvious for a person skilled in the art to combine the teachings of D8 where the velocity of the electrolyte flow is specified to be about 10 m/sec (D8, page 3, lines 14-18; page 4, lines 113 - page 5, line 4 and 20-24) with the specific pulse plating method for high-aspect ratio structures of D4 in order to optimise the plating result.

3.4 Dependent claims 3-19 seem not to contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step (Article 33 (3) PCT).

Re Item VIII

Certain observations on the international application

The relative terms "about" and "approximately" used in claims 1-6 and 9 have no well-recognised meaning and leave the reader in doubt as to the meaning of the technical features to which they refer, thereby rendering the definition of the subject-matter of said claims unclear, Article 6 PCT.

PCT/EP04/02208
Atotech Deutschland GmbH
5 August 2005

Amended Claim 1:

Method of electroplating a workpiece comprising high-aspect ratio holes, the method comprising:

a. bringing the workpiece and at least one anode into contact with a metal plating electrolyte, wherein the workpiece is brought into contact by delivering the metal plating electrolyte towards the surface of the workpiece at an electrolyte flow velocity relative to the surface of the workpiece, wherein the electrolyte flow velocity at the surface of the workpiece comprises a velocity component normal to the surface of the workpiece being at least about 1 m/sec, and

b. applying a voltage between the workpiece and the anodes, to the effect that a current flow is provided to the workpiece, wherein the current flow is a pulse reverse current flow having a frequency of at most about 6 Hertz with, in each cycle time, at least one forward current pulse and at least one reverse current pulse, the ratio of the duration of the forward current pulses to the duration of the reverse current pulses of one cycle being set to at least 5.

12. Method according to claim 11, comprising increasing, in the course of metal plating the workpiece, the ratio of the peak current density of the forward current pulses to the peak current density of the reverse current pulses, and/or decreasing, in the course of metal plating the workpiece, the ratio of the duration of the forward current pulses to the duration of the reverse current pulses of one cycle.

EPO - DG 1

26. 10. 2004

~~13. Method according to any one of the preceding claims, comprising bringing the workpiece into contact with the metal plating electrolyte by delivering the metal plating electrolyte towards the surface of the workpiece at an electrolyte flow velocity relative to the surface of the workpiece.~~

13

~~14~~. Method according to any one of the preceding claims ~~claim 13~~, comprising forcing the metal plating electrolyte under agitation towards the workpiece.

~~15. Method according to any one of claims 13 and 14, wherein the electrolyte flow velocity at the surface of the workpiece comprises a velocity component normal to the surface of the workpiece being at least about 1 m/sec.~~

14

~~16~~. Method according to any one of the preceding claims, wherein the anodes are inert and dimensionally stable.

15

~~17~~. Method according to any one of the preceding claims, wherein the metal plating electrolyte is a copper plating electrolyte.

16

~~18~~. Method according to claim ~~17~~ 15, wherein the copper plating electrolyte contains at least one compound capable of oxidizing copper metal to copper ions and wherein additional copper metal pieces are brought into contact with the copper plating electrolyte.

17

~~19~~. Method according to claim ~~18~~ 16, wherein the compounds capable of oxidizing copper metal to copper ions are ferric compounds.